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(54) Title: A NEW ALUMINUM TRIHYDROXIDE PHASE AND CATALYSTS MADE THEREFROM

(57) Abrégé/Abstract:
A newly discovered phase of aluminum trihydroxide and supports and catalysts made therefrom. This invention also relates to methods of producing this new phase of aluminum trihydroxide and catalysts made therefrom, and to a method for improving the activity of and for regenerating catalysts having a silica-alumina support.

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A NEW ALUMINUM TRIHYDROXIDE PHASE AND CATALYSTS MADE THEREFROM

Technical Field

This invention relates to a newly discovered phase of aluminum trihydroxide. This invention further relates to catalysts made from this new phase of aluminum trihydroxide, which catalysts may be specifically formulated to provide improved performance characteristics for a great number of hydrocarbon processing operations. This invention also relates to methods of producing this new phase of aluminum trihydroxide and catalysts made therefrom, and to a method of improving the activity of catalysts having a silica-alumina support.

Background Art

The art relating to alumina-containing supports, impregnating such supports with various catalytically active metals, metal compounds and/or promoters, and various uses of such impregnated supports as catalysts, is extensive and relatively well developed. As a few of the many exemplary disclosures relating to these fields, there may be mentioned the following United States Patents: U.S. Pat. Nos. 2,838,444; 2,935,463; 2,973,329; 3,032,514; 3,058,907; 3,124,418; 3,152,865; 3,232,887; 3,287,280; 3,297,588; 3,328,122; 3,493,493; 3,623,837; 3,749,664; 3,778,365; 3,897,365; 3,909,453; 3,983,197; 4,090,874; 4,090,982; 4,154,812; 4,179,408; 4,255,282; 4,328,130; 4,357,263; 4,402,865; 4,444,905; 4,447,556; 4,460,707; 4,530,911; 4,588,706; 4,591,429; 4,595,672; 4,652,545; 4,673,664; 4,677,085; 4,732,886; 4,797,196; 4,861,746; 5,002,919; 5,186,818; 5,232,888; 5,246,569; 5,248,412 and 6,015,485.

While the prior art shows a continuous modification and refinement of such catalysts to improve their catalytic activity, and while in some cases highly desirable activities have actually been achieved, there is a continuing need in the industry for even higher activity catalysts, which are provided by the present invention.

Much of the effort to develop higher activity catalysts has been directed toward developing supports that enhance the catalytic activity of metals that have been deposited thereon. In an overwhelming majority of applications the material chosen for a support is alumina, most often γ-alumina, but silica-alumina composites, zeolites and various other inorganic oxides and composites thereof have been and are employed as support materials.

In the case of alumina, various researchers have developed methods for preparing supports having various surface areas, pore volumes and pore size distributions that, when appropriate metals are applied, are particularly suited for catalyzing a desired reaction on a particular feedstock, whether that reaction be directed toward hydrodesulphurization, hydrodemetallation, hydrocracking, reforming, isomerization and the like.

In most cases, the γ-alumina supports are produced by activation (usually calcination) of pseudo-boehmite (AlOOH) starting material. On rare occasions, the support has been generated from one of the heretofore known aluminum trihydroxides ($Al(OH)_3$), Gibbsite, Bayerite or Nordstrandite. When Bayerite or Nordstrandite is used as starting material, the resulting dehydrated alumina has a structure different from the more typical γ-alumina, often referred to as η-alumina; for Gibbsite, the product alumina can be χ-alumina. Each of these transitional aluminas possesses different textures (porosities and surface areas) from the more common γ-alumina. However, they generally suffer from lower thermal stability than γ-alumina; for a specific dehydration and calcination procedure, the loss of surface area for these aluminas is much greater than would be experienced by γ-alumina. U.S. Patent No. 6,015,485 teaches a way to enhance the texture of γ-alumina supported catalysts by the in-situ synthesis of a crystalline alumina on the γ-alumina base support. From that teaching, higher activity catalysts have been produced.

As an example of the need for higher activity catalysts may be mentioned the need for a higher activity first stage hydrocracking catalyst. In a typical hydrocracking process, higher molecular weight hydrocarbons are converted to lower molecular weight fractions in the presence of a hydrocracking catalyst which is normally a noble metal impregnated silica-alumina/zeolite. State-of-the-art hydrocracking catalysts possess a very high activity and are capable of cracking high volume throughputs. Such catalysts, however, are highly sensitive to contaminants such as sulfur, metals and nitrogen compounds, which consequently must be removed from the hydrocarbon stream prior to the cracking. This is accomplished in first stage hydrocracking processes such as hydrodenitrogenation, hydrodesulfurization and hydrodemetallation. Hydrotreating catalysts utilized in these processes are typically a combination Group VIB and Group VIII metal impregnated alumina substrate. State-of-the-art hydrotreating catalysts, however, are not sufficiently active to allow processing of the same high volume throughputs as can be processed by the hydrocracking catalysts. As such, the first stage hydrocracking processes form a bottleneck in the overall hydrocracking process, which must be compensated, for example, in the size of the hydrotreating unit relative to the hydrocracking unit.

Disclosure of the Invention

In accordance with the present invention, there is provided, in one aspect, a newly discovered phase of aluminum trihydroxide that is produced by hot-aging formed and calcined silica-alumina support made from amorphous alumina-rich silica-alumina powder in an acidic, aqueous environment. This newly discovered aluminum trihydroxide phase, herein named "Kamenetsite", can be distinguished from the three previously known phases, Gibbsite, Bayerite and Nordstrandite, by X-ray Diffraction analysis. When subjected to drying and calcination, Kamenetsite forms a material that is texturally and structurally different from other supports. The catalysts made from this material exhibit exceptionally high catalytic activity in many hydrotreating and non-hydrotreating reactions. Indeed, by appropriate adjustment of the aging conditions used in the production of Kamenetsite, the final texture of the catalyst can be tailored to a specific catalytic application. There is evidence that catalysts containing the same active metals and active metals loading perform differently with certain petroleum feedstocks depending upon the size and concentration of the crystalline alumina particles produced from different Kamenetsite-containing support precursors.

Also provided in this invention is a method of making Kamenetsite from amorphous alumina-rich silica-alumina powder. This method involves process steps that are similar to those taught in an earlier patent (US 6,015,485). In the present invention, however, the starting material is different from that used in '485 and the product of the process may be distinguished by the size and concentration of the crystalline alumina particles produced and in the performance of catalysts made from the support produced.

More especially, the invention provides in one aspect, a composition comprising an aluminum trihydroxide phase having measurable X-ray diffraction lines between $2\theta = 18.15°$ and $2\theta = 18.50°$, between $2\theta = 36.1°$ and $2\theta = 36.85°$, between $2\theta = 39.45°$ and $2\theta = 40.30°$, and between $2\theta = 51.48°$ and $2\theta = 52.59°$, and not having measurable X-ray diffraction lines between $2\theta = 20.15°$ and $2\theta = 20.65°$.

In another aspect of the invention there is provided a catalyst precursor comprising the composition of the invention.

In a further aspect of the invention there is provided a catalyst comprising a support produced from the composition of the invention, or the catalyst precursor of the invention, and a catalytically active amount of one or more metals, metallic compounds, or combinations thereof.

In a particular embodiment, the present invention provides high activity catalysts comprising supports based upon Kamenetsite and impregnated with one or more metals from Group VIB and Group VIII of the Periodic Table.

In another aspect of the invention there is provided a process for making the catalyst of the invention, comprising: (a) forming a starting material comprising silica coated amorphous alumina comprising between 4 wt.% and 8 wt. % silica, wherein at least 20 wt.% of said alumina is amorphous, into a shape; (b) wetting the starting material by contact with an amount of chelating agent and a catalytically active amount of one or more metals, metallic compounds, or combinations thereof in a carrier liquid; (c) aging the so-wetted starting material while wet; (d) drying the so-aged starting material at a temperature between 100 °C and 230°C and under conditions to substantially volatilize the carrier liquid; and (e) calcining the so-dried material.

In another aspect of the invention there is provided a process for improving the catalytic activity of a silica-alumina supported catalyst comprising between 4 wt.% and 8 wt. % silica, wherein at least 20 wt.% of said alumina is amorphous, and a metal or metal compound, comprising: (a) wetting said catalyst by contact with a chelating agent in a carrier liquid; (b) aging the so-wetted catalyst while wet; (c) drying the so-aged catalyst at a temperature between 100°C and 230°C and under conditions to substantially volatilize the carrier liquid; and (d) calcining the so-dried catalyst, wherein the so-dried catalyst comprises the composition of the invention.

This latter process process for improving the activity of a catalyst composition suitably comprises employs a particulate porous support comprising the silica-alumina and amorphous alumina, and impregnated with one or more catalytically active metals. In particular such process comprising the steps of : (1) wetting the catalyst composition by contact with a chelating agent in a carrier liquid; (2) aging the so-wetted substrate while wet; (3) drying the so-aged substrate at a temperature and under conditions to substantially volatilize the carrier liquid; and (4) calcining the so-dried substrate.

This process can readily be applied to existing catalysts comprising a particulate porous support containing silica-alumina and amorphous alumina, or can be utilized in a catalyst manufacture process concurrently with and/or subsequent to the impregnation of the support containing silica-alumina and amorphous alumina, with one or more catalytically active metals and/or compounds thereof. In addition, the process can be utilized to improve the activity of spent catalysts during regeneration, which spent catalysts comprise a particulate porous support containing silica-alumina and amorphous alumina, wherein the spent catalyst is wetted as in step (1) above subsequent to the removal of carbonaceous deposits therefrom, followed by steps (2), (3) and (4).

Thus the invention also relates to a process for regenerating a previously used silica-alumina supported catalyst comprising between 4 wt.% and 8 wt. % silica, wherein at least 20 wt.% of said alumina is amorphous, and a metal or metal compound, comprising: (a) removing material deposited on said catalyst during its previous use; (b) wetting said catalyst by contact with a chelating agent in a carrier liquid; (c) aging the so-wetted catalyst while wet; (d) drying the so-aged catalyst at a temperature between 100°C and 230°C and under conditions to substantially volatilize the carrier liquid; and (e) calcining the so-dried catalyst, wherein the so-dried catalyst comprises the composition the invention and the metal or metal compound.

Still further the invention relates to a process for making a catalyst tailored to the treatment of a hydrocarbonaceous material comprising nitrogen-containing compounds, comprising: (a) determining the concentration of nitrogen-containing compounds in the hydrocarbonaceous material; (b) choosing a starting material comprising silica coated amorphous alumina comprising between 4 wt.% and 8 wt. % silica, wherein at least 20 wt.% of said alumina is amorphous, wherein said alumina has an appropriate concentration of silica so that, when wet-aged at an appropriate wet-aging temperature for an appropriate length of time forms a catalyst precursor, said catalyst precursor comprising a sufficient concentration of a composition of the invention, so that a catalyst made from said catalyst precursor will be effective in treating said hydrocarbonaceous material; wherein said appropriate concentration of silica, appropriate wet-aging temperature and appropriate length of time are chosen to be in proportion to the concentration of said nitrogen-containing compounds; (c) forming said starting material into a shape; (d) wetting said starting material by contact with a chelating agent and an amount of metal compound in a carrier liquid; (e) aging the so-wetted starting material while wet at the temperature chosen in (b) for the length of time chosen in (b); (f) drying the so-aged starting material at a temperature between 100°C and 230°C and under conditions to substantially volatilize the carrier liquid; and (g) calcining the so-dried material; wherein the catalyst comprises the composition of the invention and a metal or metal component.

By performing these steps in the indicated order, it is believed (without wishing to be bound by any particular theory) that an interaction takes place between at least the silica-alumina, amorphous alumina, chelating agent and aqueous acid which, when subjected to the temperature and time conditions of the aging step, results in the appearance of Kamenetsite. Upon drying and calcining the product from this reaction a crystalline phase of alumina that may be distinguished from that produced in US 6,015,485 by the size and concentration of the crystalline alumina particles produced. Crystallite size at the catalyst surface can be measured via well-known techniques involving transmission electron microscopy.

Concurrent with the appearance of this crystalline phase, an increase in the surface area of the catalyst is also achieved. In addition, in preferred embodiments, a structure is generated with a porosity peaking in a first region of pore size 40 Å or less, and more preferably in the range of 20 Å to 40 Å, as measured by nitrogen porosimetry using the desorption isotherm.

The resulting high activity catalysts find use in a wide variety of fields as detailed in the many previously incorporated references. A particularly preferred use is as a first stage hydrocracking catalyst in hydrodenitrogenation, hydrodesulfurization and hydrodemetallation.

These and other features and advantages of the present invention will be more readily understood by those of ordinary skill in the art from a reading of the following detailed description.

Brief Description of the Drawings

Fig. 1 shows the FTIR spectra of the aluminum trihydroxide of the present invention, aged at 90°C for 1 day and for 25 days, and of 1-day-aged material spectrum subtracted from the 25-day-aged material spectrum.

Fig. 2 shows the FTIR spectra for boehmite, Bayerite, Gibbsite and Nordstrandite.

Fig. 3 shows a 22 hour scan X-Ray Diffraction pattern for the sample aged for 25 days at 90°C. The marked lines are for Kamenetsite. Several unmarked lines present below 5A d-spacing, are due to organic species present in the oven-dried sample. There are also broad diffraction lines attributable to the γ-alumina support and the active metal oxides.

Detailed Description of the Invention

A. New Aluminum Trihydroxide Phase (Kamenetsite)

Starting Material

The preferred starting material for the production of Kamenetsite is silica-alumina powder containing a substantial percentage of amorphous alumina. A measurable concentration of Kamenetsite may be produced from powder comprising as little as 4 wt.% silica and the balance alumina, at least about 20 wt.% of which is amorphous alumina and from a powder comprising as much as 8 wt.% silica and the balance alumina, at least about 30 wt.% of which is amorphous alumina. Preferably, the starting material contains between about 5 wt.% and about 7 wt.% silica and the balance alumina, with between about 20 wt.% and about 50 wt.% of the alumina being amorphous.

Method of Making

The new aluminum hydroxide phase of this invention may be prepared by:

(1) wetting the starting material by contact with a chelating agent in a carrier liquid and an acidic solution of a metal compound;

(2) aging the so-wetted starting material while wet at conditions (i.e., a combination of temperature and duration of aging) that will produce the desired amount of Kamenetsite, preferably at temperatures higher than 50°C for from 1 to 10 days;

(3) drying the so-aged starting material at a temperature and under conditions to substantially volatilize the carrier liquid; and

(4) calcining the so-dried material.

Chelating agents suitable for use in this process include those known to form more stable complexes with transition metals and aluminum and, consequently, possess high stability constants with respect thereto. Particularly preferred for use in the present invention is ethylenediaminetetraacetic acid (EDTA) and derivatives thereof including, for example, N-hydroxy ethylenediaminetetraacetic acid and diammonium ethylenediaminetetraacetic acid. Also suitable are tris(2-aminoethyl)amine and triethylenetetraamine. Other candidates include diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, ethyleneglycol-bis-(beta-aminoethylether)-N,N'-tetraacetic acid, tetraethylenepentaamine and the like. The suitability of other chelating agents can be readily determined by those of ordinary skill in the art by treating a starting material sample in accordance with the present invention and then, prior to drying and calcining the sample, determining with the aid of transmission electron microscopy or X-ray Diffraction whether or not Kamenetsite of appropriate crystallite size has formed.

The amount of chelating agent utilized is not critical to producing Kamenetsite, but does have an influence on the amount produced. Widely varying amounts of chelating agent can be utilized depending on a number of factors such as solubility in the carrier liquid, type of catalyst support and metals impregnated or to be impregnated thereon. Generally, the starting material should be wetted by a carrier liquid containing the chelating agent in amounts ranging from 0.01-1.0 grams of chelating agent per gram of starting material.

The material may be wetted by any normal method such as dipping or spraying. To ensure adequate infiltration of the chelating agent, dipping is preferred followed by a soaking period. The preferred carrier liquid is water or a water/ammonia solution.

The length of time necessary for aging of the wet starting material is a function of the temperature during aging. At room temperature, it is preferred to age the wetted substrate for at least 30 days, more preferably at least 60 days. As temperature increases, the required aging time decreases. At 80°C., it is preferred to age the wetted material for at least two days, more preferably at least three days. Preferably, aging is accomplished at a temperature in the range of 20°C. to 90°C.

Subsequently, the aged material is dried to substantially remove the carrier liquid. It is preferred that the drying take place slowly at first and then rapidly at elevated temperatures in the range of 100°C. to 250°C. Preferably, a forced air heater is utilized to speed drying to a preferred time of less than one hour.

The so-dried material is then calcined under conditions well-known to those of ordinary skill in the art. Preferably, however, the calcination takes place in two stages--a first lower temperature stage in which the temperature is sufficiently high to drive off or decompose any remaining chelating agent, but which is not so high that the chelating agents combust to form carbonaceous deposits. This first stage temperature will vary depending on the particularly chelating agent, but typically a temperature within the range of 250°C. to 350°C. will be sufficient. Once any remaining chelating agent is substantially removed, the catalyst may then be calcined under the normal higher temperature conditions commonly utilized.

B. Catalysts

Method of Making Kamenetsite-containing Catalysts

The procedure for making Kamenetsite described above may be adapted for producing a finished catalyst. The starting material may first be formed into the desired support shape by methods known to those skilled in the art. The formed, calcined support can then be wetted with the chelating agent/carrier liquid either prior to, concurrently with and/or subsequent to the impregnation of the support with the appropriate catalytically active metals, followed by steps (2) through (4) as described above. It is only important to ensure that the aging step takes place while the impregnated support is wet from the carrier liquid for the chelating agent and the acidic solution of impregnation metals.

Catalytically Active Metals

The present invention is applicable to catalysts impregnated with one or more of a wide variety of catalytically active metals well-known to those of ordinary skill in the art as exemplified, for example, by the numerous incorporated references. In the context of the present invention, "catalytically active metals" includes both the metals themselves as well as metal compounds. In addition to the catalytically active metals, the catalysts may also be impregnated with one or more well-known promoters such as phosphorous, tin, silica and titanium (including compounds thereof).

Typically, the catalytically active metals are transition metals selected from the group consisting of Group VIB metals, Group VIII metals and combinations thereof. The specific choice of metal(s), promoter(s) and loadings, of course, depends upon the desired end use of the catalyst, and these variables can readily be adjusted by those of ordinary skill in the art based upon the end use. As specific examples thereof may be mentioned the following (wt % is based on the total catalyst weight):

Hydrotreating Operations

-Hydrodenitrogenation	Ni and/or Co, and preferably Ni, in an amount up to 7 wt % calculated as NiO and/or CoO Mo and/or W, preferably Mo, in an amount up to 35 wt.% calculated as MoO_3 and/or WO_3 optionally P, and preferably including P, in an amount up to10 wt % calculated as P_2O_5
-Hydrodesulfurization	Ni and/or Co, and preferably Co, in an amount up to 9 wt % calculated as NiO and/or CoO Mo and/or W, preferably Mo, in an amount up to 35 wt % calculated as MoO_3 and/or WO_3 optionally P, and preferably including P, in an amount up to10 wt % calculated as P_2O_5
-Hydrodemetallation	optionally Ni and/or Co, and preferably including Ni and/or Co, in an amount up to 5 wt % calculated as NiO and/or CoO Mo and/or W, preferably Mo, in an amount up to 20 wt % calculated as MoO_3 and/or WO_3 optionally P, and preferably including P, in an amount up to10 wt % calculated as P_2O_5
-Hydroconversion	Ni and/or Co, and preferably Ni, in an amount up to 5 wt % calculated as NiO and/or CoO Mo and/or W, preferably Mo, in an amount up to 20 wt % calculated as MoO_3 and/or WO_3 optionally P, and preferably including P, in an amount up to 6 wt % calculated as P_2O_5

-Hydrocracking	Ni and/or Co, and preferably Ni, in an amount up to 5 wt % calculated as NiO and/or CoO Mo and/or W, preferably Mo, in an amount up to 20 wt % calculated as MoO_3 and/or WO_3 optionally P, and preferably including P, in an amount up to 10 wt % calculated as P_2O_5
-Hydrogenation/ Dehydrogenation	a noble metal, and preferably Pt or Pt in combination with Rh, in an amount up to 2 wt % calculated on an elemental basis
-Reforming	a noble metal, and preferably Pt or Pt in combination with another noble metal such Re and/or Ir, and/or Sn, in an amount up to 2 wt % calculated on an elemental basis
<u>Non-Hydrotreating Operations</u>	
-Isomerization	a noble metal, and preferably Pt or Pt in combination with another noble metal, in an amount up to 2 wt % calculated on an elemental basis
-Claus Process	Ni and/or Co, and preferably Ni, in an amount up to 5 wt % calculated as NiO and/or CoO Mo and/or W, preferably Mo, in an amount up to 20 wt % calculated as MoO_3 and/or WO_3 optionally P, and preferably including P, in an amount up to 6 wt % calculated as P_2O_5

Such catalysts are prepared by impregnating the supports with the appropriate components, followed by various drying, sulfiding and/or calcining steps as required for the appropriate end use. Such catalyst preparation is generally well-known to those of ordinary skill in the relevant art, as exemplified by the numerous previously incorporated references, and further details may be had by reference thereto or numerous other general reference works available on the subject.

Catalyst Regeneration

As indicated above, the process in accordance with the present invention is not only applicable to pre-formed catalysts, but also can be applied to regenerated catalysts in a like manner. Specifically, subsequent to the removal of carbonaceous material from a spent catalyst via well-known procedures, such catalysts are then be treated by steps (1) through (4) in an identical manner as described above.

Catalysts Tailored to a Specific Operation

By careful selection of temperature and time during the aging step, the concentration and crystallite size of the Kamenetsite along with its ultimate pore structure can be modified. The modified catalyst then displays a different response to, for example, the hydrodesulfurization of a pair of gas oils. One possibility for tailoring a catalyst of the present invention is discussed in Example 9 below. Example 9 is meant to be illustrative of the possibilities that accrue from the present invention and is not intended to be limiting in any way. Those skilled in the art are capable of identifying other such opportunities.

C. Characterization of Kamenetsite

X-ray diffraction analysis using copper Kα radiation of crystals of the newly discovered aluminum trihydroxide phase confirm that the material is different from the three previously known phases of aluminum trihydroxide. As shown in Table 1 below, Kamenetsite exhibits a very strong peak at $2\theta = 18.33°$, the same angle as the major peak for Gibbsite and reasonably close to the major peaks of Nordstrandite and Bayerite. Across the remainder of the diffraction pattern, however, Kamenetsite shows significant peaks at diffraction angles where the other phases do not and does not show peaks at angles where they do. The positions of the Kamenetsite diffraction lines are quoted here to a relative precision of 1% (95% Confidence Index) and relative intensities to a relative precision of 10% (95% CI).

Table 1

	Relative Intensity			
Diffraction Line 2θ, °	Kamenetsite (1)	Gibbsite (2)	Nordstrandite (2)	Bayerite (2)
18.33	100	100	-----	-----
18.50	-----	-----	100	-----
18.80	-----	-----	-----	100
20.25-20.55	-----	36	30	70
27.63	3	-----	-----	-----
35.12	5	-----	-----	-----
36.47	25	-----	-----	-----
37.55	-----	-----	30	-----
39.76	-----	-----	30	-----
39.87	38	-----	-----	-----
40.50	-----	-----	-----	100
52.09	33	-----	-----	-----
63.12	6	-----	-----	-----

(1) All diffraction lines that grow with aging, indicating an increase in the concentration of the new phase, are shown.

(2) Only major diffraction lines are shown for Gibbsite, Nordstrandite and Bayerite.

Kamenetsite crystallite size and the integrated intensity of the X-ray diffraction line at $2\theta = 18.33°$ both increase with increased aging temperature and duration of aging as shown in Table 2.

Table 2

Aging Temperature, °C.	Duration of Aging, days	Crystallite Size, A	Integrated Intensity of line at $2\theta = 18.33°$, counts
90	1	35	1972
	2	48	2354
	3	55	3086
	5	61	3510
	7	64	4039
	10	72	4438
80	1	23	2165
75	3	24	1246

Thermogravimetric Analysis (TGA) and X-ray diffraction of Kamenetsite-containing materials heated to high temperatures show the disappearance of the major peak at $2\theta = 18.33°$ _at about 250°C. Since 250°C is the known transformation temperature of aluminum trihydroxides to transition aluminas, these data confirm that the new material is a distinct new phase of aluminum trihydroxide.

In addition, Fourier Transform Infra-Red (FTIR) spectroscopy analysis has been carried out on the 90°C, 1-day-aged and 25-day-aged low-temperature dried products. These spectra are shown in Figure 1. The enhanced presence of Kamenetsite in the 25-day-aged material is clearly seen when the 1-day-aged material spectrum is subtracted from the 25-day-aged material spectrum, shown as the "difference" spectrum at the bottom of Figure 1. FTIR bands at 3512, 989, and 521 wave numbers in the "difference" spectrum confirm the presence of $Al(OH)_3$.

For comparison, the FTIR spectra of boehmite, Bayerite, Gibbsite and Nordstrandite are shown in Figure 2.

Comparison with Material Produced without Silica in the Starting Material

The appearance of Kamenetsite in material produced by the process of the present invention is not readily apparent when the starting material contains less than about 4 wt.% silica. A correlation has been developed, however, that permits the indirect determination of the amount of Kamenetsite contained in the product of the process of the present invention. This correlation relates the amount of Kamenetsite in a product to its texture as determined by its porosity measured by the adsorption of nitrogen. Based upon an extrapolation of this correlation, it is possible to conclude that a small amount of Kamenetsite is probably present in material produced using silica-free alumina as a starting material. The data showing these extrapolated values for Kamenetsite in materials produced from such silica-free alumina are shown in Examples D and E.

Examples

The present invention as described above will be further exemplified by the following specific examples which are provided by way of illustration and not limitation thereof.

Test Conditions

Test conditions used in comparing the performance of catalysts of the present invention against those of US 6,015,485 and a standard refinery catalyst are:

Test Type A

Feedstock:	Straight-run gas oil for North American refiner.	
	Sulfur, wt.%:	1.25
	Total Nitrogen, ppm	65
	Density, g/cc	0.848
	Aromatics, wt.%	8.63
	Diaromatics, wt.%	2.63
	Distillation, °C:	
	Initial	114.5
	50 %	286.7
	95 %	368.9

Test Conditions:

Temperature, °C	343
Pressure, kPa (psig)	4,169 (590)
Gas Rate, m^3/m^3 (SCF/B)	178.1 (1000)
Liquid Hourly Space Velocity (LHSV), hr^{-1}	2

<u>Test Type B</u>

Feedstock: Straight-run light Arabian gas oil for European refiner.

Sulfur, wt.%:	1.77
Total Nitrogen, ppm	183
Density, g/cc	0.863
Aromatics, wt.%	12.94
Diaromatics, wt.%	4.46
Distillation, °C:	
Initial	175
50 %	290.6
95 %	366.7

Test Conditions:

Temperature, °C	360
Pressure, kPa (psig)	4,155 (588)
Gas Rate, m^3/m^3 (SCF/B)	178.1 (1000)
Liquid Hourly Space Velocity (LHSV), hr^{-1}	1, 2 and 3

<u>Test Types C_1, C_2, C_3</u>

Feedstock: Gas Oil blend

Sulfur, wt.%:	1.637
Total Nitrogen, ppm	401
Density, g/cc	0.887

Test Conditions:

Temperature, °C	C_1 = 343; C_2 = 357; C_3 = 371
Pressure, kPa (psig)	4,755 (675)
Gas Rate, m^3/m^3 (SCF/B)	213.7 (1200)
Liquid Hourly Space Velocity (LHSV), hr^{-1}	2.7

<u>Test Type D</u>

Feedstock: Straight-Run/Light Cycle Gas Oil blend

Sulfur, wt.%:	0.8
Total Nitrogen, ppm	196
Density, g/cc	0.889

Test Conditions:

Temperature, °C	349
Pressure, kPa (psig)	4,100 (580)
Gas Rate, m^3/m^3 (SCF/B)	178.1 (1000)
Liquid Hourly Space Velocity (LHSV), hr^{-1}	2.0

<u>Test Types E_1, E_2</u>

Feedstock:	Straight-Run/Light Cycle Gas Oil blend	
	Sulfur, wt.%:	0.508
	Total Nitrogen, ppm	760
	Density, g/cc	0.859
	Test Conditions:	
	Temperature, °C	$E_1 = 343$; $E_2 = 385$
	Pressure, kPa (psig)	4,928 (700)
	Gas Rate, m^3/m^3 (SCF/B)	178.1 (1000)
	Liquid Hourly Space Velocity (LHSV), hr^{-1}	2.4

<u>Test Type F</u>

Feedstock:	Straight-Run Light Arabian Gas Oil	
	Sulfur, wt.%:	1.005
	Total Nitrogen, ppm	251
	Density, g/cc	0.864

Test Conditions:

Temperature, °C	363
Pressure, kPa (psig)	4,100 (580)
Gas Rate, m^3/m^3 (SCF/B)	178.1 (1000)
Liquid Hourly Space Velocity (LHSV), hr^{-1}	3.0

Example 1

This example describes the preparation of samples of catalysts of the present invention.

A powder comprising alumina particles coated with 6 wt. % silica was mulled, extruded into a trilobe shape, dried and calcined by conventional means. Details of the 6 wt.% silica-alumina powder has been described in the open literature (McMillan M., Brinen, J.S., Carruthers, J.D. and Haller, G.L., " A ^{29}Si NMR Investigation of the Structure of Amorphous Silica-Alumina Supports", Colloids and

Surfaces, 38 (1989) 133-148). The powder used here met the criterion for porosity stability as described in the above publication.

95.6 grams of the silica-alumina support was impregnated to incipient wetness with 100 ml of solution “A”. The solution, designated herein as solution “A”, consisted of a mixture of two solutions: solution “C” prepared by adding 11.3 grams of ammonium hydroxide solution (28 wt.%) to 65.3 grams of Dow Versene, Tetraammonium ethylenediaminetetraacetic acid solution (38.0% as EDTA) and solution “D”. Solution “D” was prepared by adding 4.37 grams of ammonium hydroxide solution (28 wt.%) to 41.0 grams of solution “E”. The solution, designated herein as solution “E”, was prepared by adding 137 grams of cobalt carbonate solid to 500 grams of a dilute solution of phosphoric acid (23.0 grams of H_3PO_4 - 86.0 wt.% - and 475 grams of deionized water), heating the mixture to 55°C and then adding 300 grams of Climax MoO_3. The mixture was then heated to 98°C with stirring for 1.5 hrs at which point 100 grams of nitric acid solution (70 wt.%) were added to fully dissolve the mix. This solution, designated herein as Solution “E”, of phosphoric acid containing cobalt and molybdenum compounds wherein the Co/Mo weight ratio was 0.258 and having a pH of approximately 0.6 was then cooled to room temperature and 41.0 grams of the solution were used to prepare solution designated herein as solution “D”.

The wet pills were allowed to stand for 2 hours and then dried in an oven in a shallow layer at 230°C for 1 hour. 122.6 grams of dried product were then dipped into a container of solution “E” and 360 grams of this solution were then circulated to wash the pills. The wet pills were then separated from the excess solution by centrifugation and placed in a sealed bottle in an oven set at 75°C and held at that temperature for 3 days. The material was then fast-dried at 230°C for 20 minutes to volatilize the carrier liquid to an LOI of 30 - 32 wt.%, followed by calcination at 500°C for one hour in air to produce a catalyst of the present invention, designated herein as Catalyst C-2. Catalyst C-2 contained 5.97 wt. % Co, 19.7 wt. % Mo and 0.77 wt. % P and had a surface area of 305 m^2/g and estimated Kamenetsite intensity of 3344 counts.

A second 100 gram portion of the support was wetted to incipient wetness with a solution comprising 62.5 grams of Dow Versene diammonium ethylenediaminetetraacetic acid solution (40.0 wt.% as EDTA) and 77.59 grams of solution designated herein as solution "F". Solution "F" was prepared by adding 329 grams of MoO_3, 100.0 grams of $Co(OH)_2$ and 282.6 grams of citric acid monohydrate to 695 grams of deionized water and heated from room temperature to 80°C. The solution was then boiled for approximately one hour until all components became fully dissolved and then cooled to room temperature. Solution "F" contained cobalt and molybdenum compounds wherein the Co/Mo weight ratio was 0.292 with a pH of approximately 0.6. The wet pills were allowed to soak for one hour followed by drying in a shallow layer in a dryer at 230°C for one hour.

The dried pills were then immersed in 300 grams of solution "F" and the solution circulated over the pills for one hour. The wet pills were separated from the solution by centrifugation and placed in a sealed bottle in an oven set at 75°C for 3 days. The material was then fast-dried at 230°C for 1 hour to volatilize the carrier liquid to an LOI of 30 -32 wt.%, and then calcined at 500°C for I hour to produce a catalyst of the present invention, designated herein as Catalyst D-2. Catalyst D-2 contained 4.11 wt. % Co and 16.3 wt. % Mo and had a surface area of 347 m^2/g and estimated Kamenetsite intensity of 4320 counts.

A third 100 gram portion of the support was wetted to incipient wetness with a solution containing 64.7 grams of Dow Versene diammonium ethylenediaminetetraacetic acid (40.0 wt.% as EDTA) with 82.3 grams of a solution, designated herein as Solution "G". Solution "G" was prepared by adding 300 grams of MoO_3 and 137.5 grams of $CoCO_3$ to 575 grams of deionized water followed by heating to 70- 80°C with stirring, and then adding slowly 225.0 grams of citric acid monohydrate. The solution was then boiled to complete dissolution for 30 minutes and then allowed to cool. Solution "G", containing cobalt and molybdenum compounds wherein the Co/Mo weight ratio was 0.321 had a pH of approximately 2.0. The wet pills were allowed to stand for 1 hour and then dried in a shallow layer in an oven set at 230°C for an hour.

The dried pills were then immersed in 300 grams of solution "G" and the solution circulated over the pills for one hour. The wet pills were separated from the solution by centrifugation and placed in a sealed bottle in an oven set at 75°C for 3 days. The material was then fast-dried at 230°C for one hour to volatilize the carrier liquid to an LOI of 30 -32 wt.%, and then calcined at 500°C for an additional hour to produce a catalyst of the present invention, designated herein as Catalyst E-2. Catalyst E-2 contained 4.53 wt. % Co and 14.6 wt. % Mo and had a surface area of 310 m^2/g and estimated Kamenetsite intensity of 1082 counts.

Example 2
(Comparative)

This example describes the preparation of samples of catalysts of US Patent No. 6,025,485.

A support was made using the same procedure as in Example 1, except that the starting material contained no silica.

A portion of this support was treated in the same manner as Catalyst C-2 to yield Catalyst C-1. Catalyst C-1 contained 4.67 wt. % Co, 18.1 wt. % Mo and 0.61 wt. % P and had a surface area of 280 m^2/g and estimated Kamenetsite intensity of 195 counts.

A second portion of this support was treated in the same manner as Catalyst D-2 to yield Catalyst D-1. Catalyst D-1 contained 4.08 wt. % Co and 14.7 wt. % Mo and had a surface area of 230 m^2/g and estimated Kamenetsite intensity of less than 100 counts.

Example 3
(Comparative)

This example describes the preparation of two catalysts prepared by the method of the present invention but with insufficient and with marginally sufficient silica in the starting material to produce a catalyst of the present invention.

A support was made using the same procedure as in Example 1, except that the starting material contained 2 wt. % silica. This support was treated in the same manner as Catalyst E-2 to yield Catalyst E-1. Catalyst E-1 contained 5.91 wt. % Co and 19.7 wt. % Mo and had a surface area of 215 m^2/g and estimated Kamenetsite intensity of 300 counts.

A second support was made using the same procedure as in Example 1, except that the starting material contained 3.7 wt. % silica, lower than the preferred (6 wt. %) yet higher than the 2 wt. % used for Catalyst E-1. This support was treated in the same manner as Catalyst D-2 to yield Catalyst D-3. Catalyst D-3 contained 4.08 wt. % Co and 15.7 wt. % Mo and had a surface area of 245 m2/g and estimated Kamenetsite intensity of 1880 counts.

Example 4

This example compares the performance of Catalyst C-2 to Catalyst C-1 and a refinery standard catalyst ("Standard"), manufactured by conventional means.

Each catalyst was subjected to Test Type A. The results are presented in Table 3:

Table 3

Catalyst	$S_{product}$, wppm	RVA (1)
Standard	330	100
C-1	175	143
C-2	91	202

(1) Relative Volume Activity (RVA) is the ratio of the rate constants for the catalysts determined from the concentration of sulfur in the product.

This test shows that Catalyst C-2, that of the present invention, is more effective at removing sulfur than either of the other two catalysts.

Example 5

This example compares the performance of Catalyst D-2 to Catalyst D-1 and a refinery standard catalyst ("Standard"), manufactured by conventional means.

Each catalyst was subjected to Test Type B. The results are presented in Table 4:

Table 4

Catalyst	$S_{product}$, wppm	RVA (1)
Standard	350	100
D-1	350	117
D-2	350	143

(1) Relative Volume Activity (RVA) is the ratio of the LHSV necessary to achieve 350 wppm sulfur in the product.

This test shows that a lesser amount of Catalyst D-2 of the present invention is required to achieve a desired sulfur level in the product than either of the other two catalysts.

Example 6

This example compares the performance of Catalyst E-2 to Catalyst E-1 and a refinery standard catalyst ("Standard"), manufactured by conventional means.

Each catalyst was subjected to Test Type B. The results are presented in Table 5:

Table 5

Catalyst	$S_{product}$, wppm	RVA (1)
Standard	350	100
E-1	350	102
E-2	350	124

(1) Relative Volume Activity (RVA) is the ratio of the LHSV necessary to achieve 350 wppm sulfur in the product.

This test shows that a lesser amount of Catalyst E-2 of the present invention is required to achieve a desired sulfur level in the product than either of the other two catalysts. The test also shows that the use of a starting material containing insufficient silica in the catalyst preparation procedure of the present invention produces a catalyst, i.e., Catalyst E-1, that is no more effective than a standard refinery catalyst.

Example 7

This example describes the preparation of samples of catalysts of the present invention in which both Ni and Co are included in the finished catalyst and the preparations are subjected to significantly different aging conditions.

100 grams of the silica-alumina support described in Example 1 was impregnated to incipient wetness with 152.4 grams of solution "K". The solution, designated herein as solution "K" consisted of a mixture of two solutions: 68.0 grams of solution "L" prepared by adding 6.66 grams of solid nickel acetate (23.58 wt. % Ni metal) to 99.54 grams of Dow Versene diammonium ethylenediaminetetraacetic acid solution (40 wt. % as EDTA) and 84.4 grams of solution "F" described in Example 1, above.

The wet pills were allowed to stand for 2 hours as before and then dried in an oven in a shallow layer at 230°C for 1 hour. 143.8 grams of dried product were then dipped into a container of solution "F" and 317 grams of this solution were then circulated to wash the pills. The wet pills were then separated from the excess solution by centrifugation and placed in a sealed bottle in an oven set at 75°C and held at that temperature for 3 days. The material was then fast-dried at 230°C for 20 minutes to volatilize the carrier liquid to an LOI of 30 - 32 wt.%, followed by calcination at 500°C for one hour in air to produce a catalyst of the present invention, designated herein as Catalyst A. Catalyst A contained 4.3 wt.% Co, 17.0 wt. % Mo and 0.68 wt. % Ni and had a surface area of 347 m^2/g and estimated Kamenetsite intensity of 2670 counts.

A second preparation followed the identical scheme for Catalyst A but was aged at 90°C for 7 days instead of the 75°C for 3 days. This catalyst was designated herein as Catalyst B. Catalyst B contained 4.24 wt.% Co, 16.8 wt. % Mo and 0.68 wt. % Ni and had a surface area of 340 m^2/g and estimated Kamenetsite intensity of 6138 counts.

Example 8

This example demonstrates that the activity of a catalyst of the present invention improves relative to that of a refinery standard catalyst as operating conditions are intensified.

Catalyst A and a refinery standard catalyst ("Standard"), manufactured by conventional means, were each subjected to Test Types C_1, C_2 and C_3, which were identical except that operating temperature increased from C_1 through C_3. The test results are presented in Table 6.

Table 6

Catalyst	Test Type					
	C_1		C_2		C_3	
	RVA-HDS (1)	$S_{product}$	RVA-HDS (1)	$S_{product}$	RVA-HDS (1)	$S_{product}$
Standard	100	797	100	420	100	209
A	132	584	144	261	159	112

(1) Relative Volume Activity (RVA) is the ratio of the rate constants for the catalysts determined from the concentration of sulfur in the product.

Note the increase in the relative volume activity as operating temperature is increased from 343°C to 357°C to 371°C. These data show that the performance of a catalyst of the present invention relative to that of a refinery standard catalyst increases as operating conditions are intensified.

Example 9

This example illustrates the ability to tailor catalysts of the present invention to the operating conditions that are expected.

Catalyst A, Catalyst B and a refinery standard catalyst ("Standard"), manufactured by conventional means, were each subjected to Test Types D, E_1 and E_2. The feedstock for Test Type D contained a moderate concentration of nitrogen (196 wppm), whereas the feedstock for Test Types E_1 and E_2 had a high nitrogen content (760 wppm).

In this example the performance the Catalyst A of the invention is contrasted with the performance of Catalyst B prepared with a much higher concentration of Kamenetsite in its precursor material. This increase in Kamenetsite was achieved by increasing both the temperature and the time during the aging step. This enhanced aging increased the concentration and the crystallite size of the Kamenetsite. Along with the change in Kamenetsite, the pore structure of the final catalyst underwent significant change. The modified catalyst then displayed a quite different response to an increase in temperature during hydrodesulfurization of just one of the gas oils. This can be seen in the following test results, presented in Table 7.

Table 7

Catalyst	Test Type					
	D		E_1		E_2	
	RVA-HDS (1)	$S_{product}$	RVA-HDS (1)	$S_{product}$	RVA-HDS (1)	$S_{product}$
Standard	100	224	100	313	100	51
A	123	159	121	234	100	55
B	130	143	128	213	131	34

(1) Relative Volume Activity (RVA) is the ratio of the rate constants for the catalysts determined from the concentration of sulfur in the product.

In this Table the three catalysts are listed with a minimal amount of description the industry-standard Reference Catalyst, Catalyst A, a catalyst of the invention prepared so that it displays a moderate concentration of Kamenetsite in the precursor material and Catalyst B, a catalyst displaying a high concentration of Kamenetsite in its precursor material. Each catalyst was then tested alongside the others at constant temperature and pressure using two Straight-Run/Light Cycle Gas Oil blends as described in Test Type D and E. G1 and G2.

Under Test Type D, both catalysts of the present invention are more active than the Standard with the higher Kamenetsite catalyst slightly better of the other (130 vs. 123 RVA). A similar result is achieved for Test Type E_1. However, notice that when the processing conditions are changed for the three catalysts in Test Type E_2, the higher Kamenetsite-version maintains its performance advantage but that of the lower concentration version falls back.

Without wishing to be bound by any particular theory, it is believed that catalysts prepared from materials high in Kamenetsite possess more active sites per unit volume of catalyst than conventionally prepared catalysts. In the example shown above, the two catalysts of the invention responded differently to an increase in temperature during Test Type E_2. The Test Type E feedstock differed from the Test Type D gas oil primarily in the concentration of nitrogen-containing molecules.

Under the low pressure and low hydrogen treat-rate conditions of these tests, removal of nitrogen-containing molecules is far from complete. In addition, the unconverted nitrogen-containing molecules become hydrogenated (basic) nitrogen molecules during partial (incomplete) hydrodenitrogenation of the gas oil. Such molecules are known to reduce the activity of the desulfurization catalyst by adsorption on its more acidic sites. It is therefore reasonable to propose that the catalyst achieving more removal of nitrogen-containing molecules (Catalyst B) and possessing more available HDS sites, will lessen the 'dynamic poisoning effect' of the remaining nitrogen-containing molecules and thereby maintain a higher hydrodesulfurization activity in the catalyst. These data therefore indicate that catalysts of the invention could be tailored for optimum performance depending upon the different concentrations of nitrogen-containing molecules in the feedstock.

Example 10

This example compares the performance of a catalyst prepared with a "sufficient" level of silica in the silica-alumina and a catalyst prepared with a "marginally sufficient" level of silica in the silica-alumina support. Catalyst D-2 is compared to Catalyst D-3 and a refinery standard catalyst ("Standard"), manufactured by conventional means, in a standard test, Test Type F.

Table 8

Catalyst	$S_{product}$, wppm	RVA (1)
Standard	212	100
D-2	117	140
D-3	161	117

(1) Relative Volume Activity (RVA) is the ratio of the rate constants for the catalysts determined from the concentration of sulfur in the product.

This test shows that the use of a starting material containing marginally sufficient silica in the catalyst preparation procedure of the present invention produces a catalyst, i.e., Catalyst D-3, that is more effective than a standard refinery catalyst but is not as active as the catalyst with sufficient silica in the silica-alumina support, Catalyst D-2

CLAIMS:

1. A composition comprising an aluminum trihydroxide phase having measurable X-ray diffraction lines between 2θ =18.15° and 2θ =18.50°, between 2θ = 36.1° and 2θ = 36.85°, between 2θ = 39.45° and 2θ = 40.30°, and between 2θ = 51.48° and 2θ = 52.59°, and not having measurable X-ray diffraction lines between 2θ = 20.15° and 2θ = 20.65°.

2. The composition of Claim 1, further characterized in that the aluminum trihydroxide phase has measurable X-ray diffraction lines between 2θ = 27.35° and 2θ = 27.90°, between 2θ = 34.75° and 2θ =35.48°, and between 2θ = 62.40° and 2θ = 63.80°.

3. The composition of Claim 1 or 2, further characterized in that the aluminum trihydroxide phase does not have measurable X-ray diffraction lines between 2θ = 20.15° and 2θ = 20.65° and between 2θ = 37.35° and 2θ = 37.75°.

4. The composition of any one of Claims 1 to 3, further characterized in that the aluminum trihydroxide phase does not have measurable X-ray diffraction lines between 2θ = 18.70° and 2θ = 18.90°, between 2θ = 20.30° and 2θ = 20.50°, and between 2θ = 40.30° and 2θ = 40.70°.

5. A catalyst precursor comprising the composition of any one of Claims 1 to 4.

6. A process for making the composition of any one of Claims 1 to 4, or the catalyst precursor of Claim 5, comprising:
(a) wetting a starting material comprising silica coated amorphous alumina comprising between 4 wt.% and 8 wt. % silica, wherein at least 20 wt.% of said alumina is amorphous, by contact with an amount of chelating agent in a carrier liquid and a metallic compound;
(b) aging the so-wetted starting material while wet;
(c) drying the so-aged starting material at a temperature between 100 °C and 230°C and under conditions to substantially volatilize the carrier liquid; and
(d) calcining the so-dried material.

7. The process of Claim 6, wherein the starting material comprises less than 8 wt. % silica and at least 30 wt. % of the alumina is amorphous.

8. The process of Claim 6, wherein the starting material comprises between 5 wt.% and 7 wt. % silica and between 20 wt. % and 50 wt. % of the alumina is amorphous.

9. The process of any one of Claims 6 to 8, wherein the chelating agent is selected from: ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylenediaminetetraacetic acid, diammonium ethylenediaminetetraacetic acid, tris(2-aminoethyl)amine, triethylenetetraamine, diethylenetriaminepentaacetic acid, cyclohexane-diaminetetraacetic acid, ethyleneglycol-bis-(beta-aminoethylether)-N,N'-tetraacetic acid or tetraethylenepentaamine.

10. The process of any one of Claims 6 to 9, wherein the amount of chelating agent is between 0.1 g and 1.0 g per g of the starting material.

11. The process of any one of Claims 6 to 10, wherein aging of the so-wetted starting material while wet is done at room temperature for at least 30 days.

12. The process of any one of Claims 6 to 11, wherein aging of the so-wetted starting material while wet is done at a temperature of at least 80°C for at least 2 days.

13. A catalyst comprising a support produced from the composition of any one of Claims 1 to 4, or the catalyst precursor of Claim 5, and a catalytically active amount of one or more metals, metallic compounds, or combinations thereof.

14. The catalyst of Claim 13, wherein the one or more metals, metallic compounds, or combinations thereof are selected from the catalytically active transition metals of Group VIB and Group VIII of the Periodic Table, compounds thereof and combinations of such metals and compounds.

15. The catalyst of Claim 13 or 14, wherein the catalyst further comprises a promoter.

16. The catalyst of Claim 15, wherein the promoter is selected from phosphorus, phosphorus compounds, and combinations thereof.

17. The catalyst of any one of Claims 13 to 16, wherein the one or more metals, metallic compounds, or combinations thereof are selected from nickel, cobalt, molybdenum, and tungsten, compounds thereof and combinations of such metals and compounds.

18. The catalyst of Claim 17, wherein the one or more metals, metallic compounds, or combinations thereof comprise molybdenum or molybdenum compounds in an amount up to 35 wt. % calculated as MoO_3, cobalt or cobalt compounds in an amount up to 9 wt. % calculated as CoO.

19. The catalyst of Claim 18, further comprising phosphorus, phosphorus compounds, or combinations thereof in an amount up to 10 wt.% calculated as P_2O_5, wherein wt. % is based on the total catalyst weight.

20. The catalyst of Claim 17, wherein the one or more metals, metallic compounds, or combinations thereof comprise molybdenum or molybdenum compounds in an amount up to 35 wt. % calculated as MoO_3, and nickel or nickel compounds in an amount up to 7 wt. % calculated as NiO.

21. The catalyst of Claim 20, further comprising phosphorus, phosphorus compounds, or combinations thereof in an amount up to 10 wt.% calculated as P_2O_5, wherein wt. % is based on the total catalyst weight.

22. The catalyst of Claim 17, wherein the one or more metals, metallic compounds, or combinations thereof comprise molybdenum or molybdenum compounds in an amount up to 20 wt. % calculated as MoO_3, and at least one of nickel, cobalt and compounds thereof, in an amount up to 5 wt. % calculated as NiO or CoO.

23. The catalyst of Claim 22, further comprising phosphorus, phosphorus compounds, or combinations thereof in an amount up to 10 wt.% calculated as P_2O_5, wherein wt. % is based on the total catalyst weight.

24. The catalyst of Claim 22, further comprising phosphorus, phosphorus compounds, and combinations thereof in an amount up to 6 wt.% calculated as P_2O_5, wherein wt. % is based on the total catalyst weight.

25. The catalyst of Claim 14, wherein the one or more metals is one or more noble metals in an amount up to 2 wt. % based on the total catalyst weight.

26. The catalyst of Claim 25, wherein the noble metal is Pt or a combination of Pt and Rh.

27. A process for treating a hydrocarbonaceous material comprising contacting said hydrocarbonaceous material with the catalyst of Claim 13.

28. A process for the catalytic hydrodesulfurization of a hydrocarbon-containing feed comprising contacting the feed under hydrodesulfurization conditions with the catalyst of Claim 18 or 19.

29. A process for the catalytic hydrodenitrogenation of a hydrocaxbon-containing feed comprising contacting the feed under hydrodenitrogenation conditions with the catalyst of Claim 20 or 21.

30. A process for the catalytic hydrodemetallation of a hydrocarbon-containing feed comprising contacting the feed under hydrodemetallation conditions with the catalyst of any one of Claims 22 to 24.

31. A process for the catalytic hydrocracking of a hydrocarbon-containing feed comprising contacting the feed under hydrocracking conditions with the catalyst of any one of Claims 22 to 24.

32. A process for the catalytic hydroconversion of a hydrocarbon-containing feed comprising contacting the feed under hydroconversion conditions with the catalyst of any one of Claims 22 to 24.

33. A process for the catalytic reforming of a hydrocarbon-containing feed comprising contacting the feed under reforming conditions with the catalyst of Claim 25.

34. A process for the catalytic hydrogenation-dehydrogenation of a hydrocarbon-containing feed comprising contacting the feed under hydrogenation-dehydrogenation conditions with the catalyst of Claim 26.

35. A process for the catalytic isomerization of a hydrocarbon-containing feed comprising contacting the feed under isomerization conditions with the catalyst of Claim 25.

36. A process for making the catalyst of Claim 13, comprising:
(a) forming a starting material comprising silica coated amorphous alumina comprising between 4 wt.% and 8 wt. % silica, wherein at least 20 wt.% of said alumina is amorphous, into a shape;
(b) wetting the starting material by contact with an amount of chelating agent and a catalytically active amount of one or more metals, metallic compounds, or combinations thereof in a carrier liquid;
(c) aging the so-wetted starting material while wet;
(d) drying the so-aged starting material at a temperature between 100 °C and 230°C and under conditions to substantially volatilize the carrier liquid; and
(e) calcining the so-dried material.

37. The process of Claim 36, wherein the starting material comprises less than 8 wt. % silica; and at least 30 wt. % of the alumina is amorphous.

38. The process of Claim 36, wherein the starting material comprises between 5 wt.% and 7 wt. % silica; and between 20 wt. % and 50 wt. % of the alumina is amorphous.

39. The process of any one of Claims 36 to 38, wherein the chelating agent is selected from ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylenediaminetetraacetic acid, diammonium ethylenediaminetetraacetic acid, tris(2-aminoethyl)amine, triethylenetetraamine, diethylenetriaminepentaacetic acid, cyclohexane-diaminetetraacetic acid, ethyleneglycol-bis-(beta-aminoethylether)-N,N'-tetraacetic acid, or tetraethylenepentaamine.

40. The process of any one of Claims 36 to 39, wherein the amount of chelating agent is between 0.1 g and 1.0 g per g of the starting material.

41. The process of any one of Claims 36 to 40, wherein aging of the so-wetted starting material while wet is done at room temperature for at least 30 days.

42. The process of any one of Claims 36 to 40, wherein aging of the so-wetted starting material while wet is done at a temperature of at least 80°C for at least 2 days.

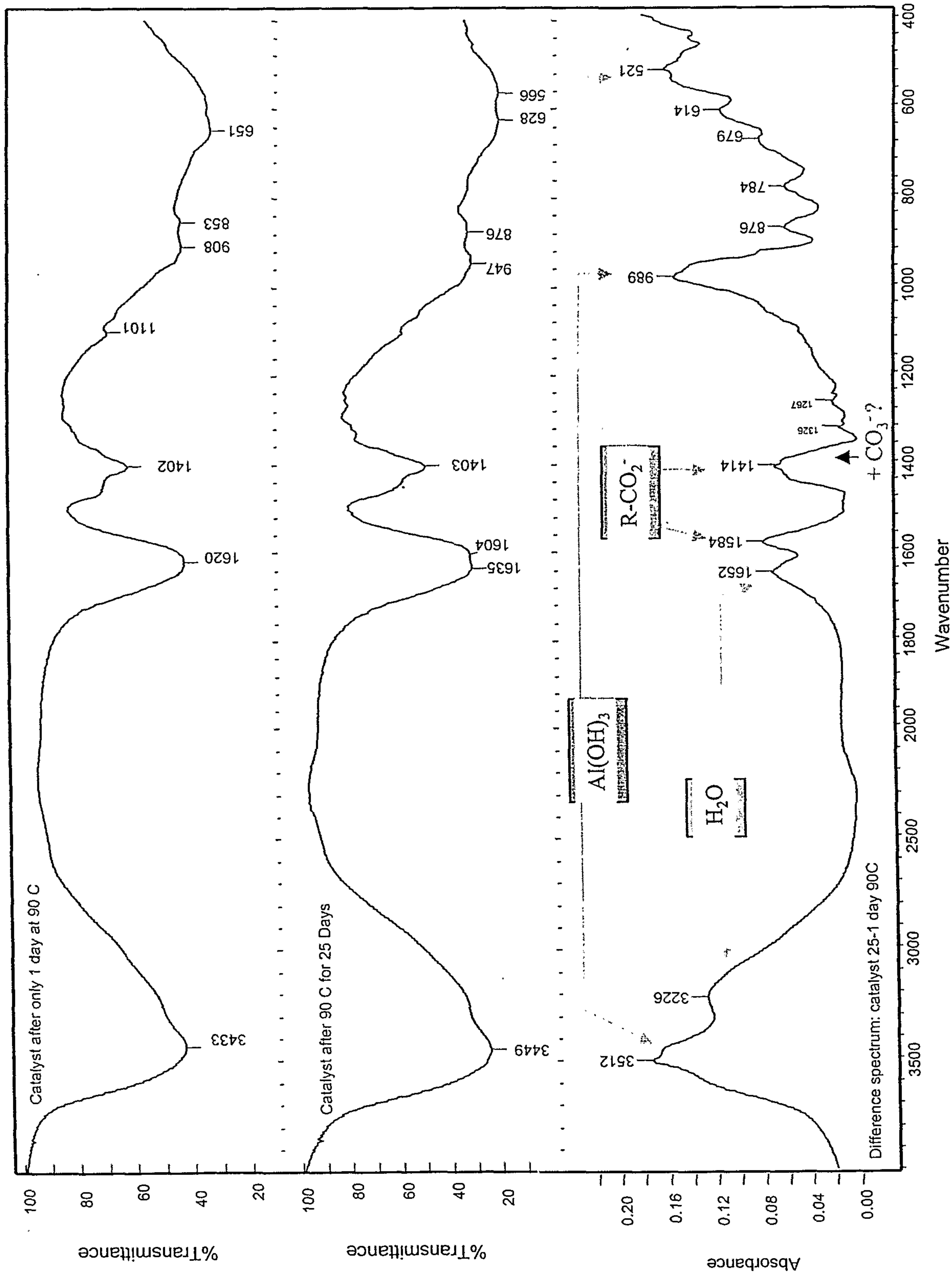
43. A process for improving the catalytic activity of a silica-alumina supported catalyst comprising between 4 wt.% and 8 wt. % silica, wherein at least 20 wt.% of said alumina is amorphous, and a metal or metal compound, comprising:
(a) wetting said catalyst by contact with a chelating agent in a carrier liquid;
(b) aging the so-wetted catalyst while wet;
(c) drying the so-aged catalyst at a temperature between 100°C and 230°C and under conditions to substantially volatilize the carrier liquid; and
(d) calcining the so-dried catalyst, wherein the so-dried catalyst comprises the composition of any one of claims 1 to 4.

44. A process for regenerating a previously used silica-alumina supported catalyst comprising between 4 wt.% and 8 wt. % silica, wherein at least 20 wt.% of said alumina is amorphous, and a metal or metal compound, comprising:
(a) removing material deposited on said catalyst during its previous use;
(b) wetting said catalyst by contact with a chelating agent in a carrier liquid;
(c) aging the so-wetted catalyst while wet;
(d) drying the so-aged catalyst at a temperature between 100°C and 230°C and under conditions to substantially volatilize the carrier liquid; and

(e) calcining the so-dried catalyst, wherein the so-dried catalyst comprises the composition as claimed in any one of claims 1 to 4 and the metal or metal compound.

45. A process for making a catalyst tailored to the treatment of a hydrocarbonaceous material comprising nitrogen-containing compounds, comprising:
(a) determining the concentration of nitrogen-containing compounds in the hydrocarbonaceous material;
(b) choosing a starting material comprising silica coated amorphous alumina comprising between 4 wt.% and 8 wt. % silica, wherein at least 20 wt.% of said alumina is amorphous, wherein said alumina has an appropriate concentration of silica so that, when wet-aged at an appropriate wet-aging temperature for an appropriate length of time forms a catalyst precursor, said catalyst precursor comprising a sufficient concentration of a composition comprising an aluminum trihydroxide phase having measurable X-ray diffraction lines between $2\theta = 18.15°$ and $2\theta = 18.50°$, between $2\theta = 36.1°$ and $2\theta = 36.85°$, between $2\theta = 39.45°$ and $2\theta = 40.30°$, and between $2\theta = 51.48°$ and $2\theta = 52.59°$, and not having measurable X-ray diffraction lines between $2\theta = 20.15°$ and $2\theta = 20.65°$ so that a catalyst made from said catalyst precursor will be effective in treating said hydrocarbonaceous material; wherein said appropriate concentration of silica, appropriate wet-aging temperature and appropriate length of time are chosen to be in proportion to the concentration of said nitrogen-containing compounds;
(c) forming said starting material into a shape;
(d) wetting said starting material by contact with a chelating agent and an amount of metal compound in a carrier liquid;
(e) aging the so-wetted starting material while wet at the temperature chosen in (b) for the length of time chosen in (b);
(f) drying the so-aged starting material at a temperature between 100°C and 230°C and under conditions to substantially volatilize the carrier liquid; and
(g) calcining the so-dried material; wherein the catalyst comprises the composition as claimed in any one of claims 1 to 4, and a metal or metal component.

FIG 1.


Catalyst after only 1 day at 90 C
Catalyst after 90 C for 25 Days
Difference spectrum: catalyst 25-1 day 90C
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%Transmittance
Absorbance
Wavenumber
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H2O
R-CO2-
+ CO3-?
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908
853
651
3449
1635
1604
1403
947
876
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784
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614
521

FIG 2.

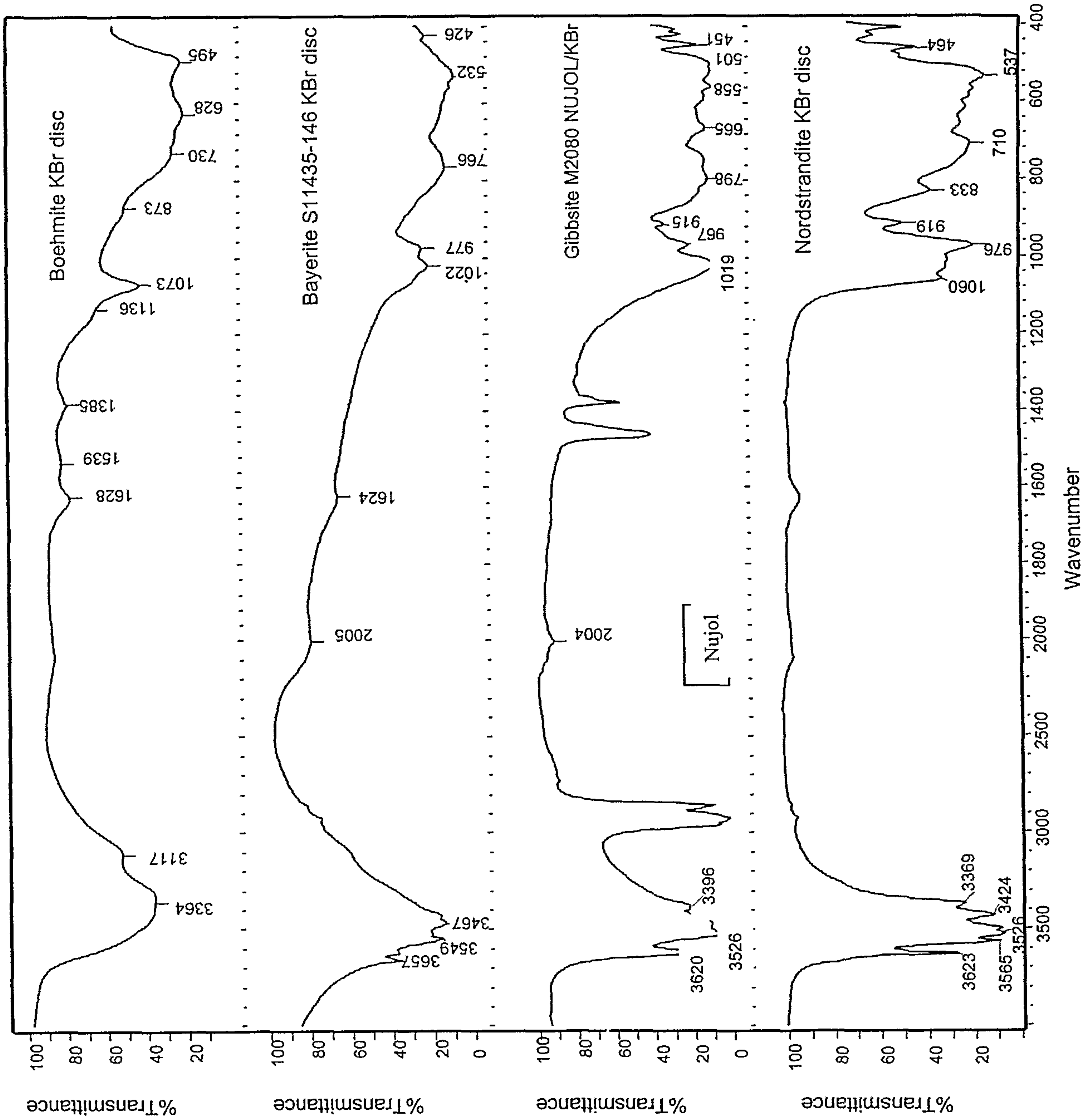
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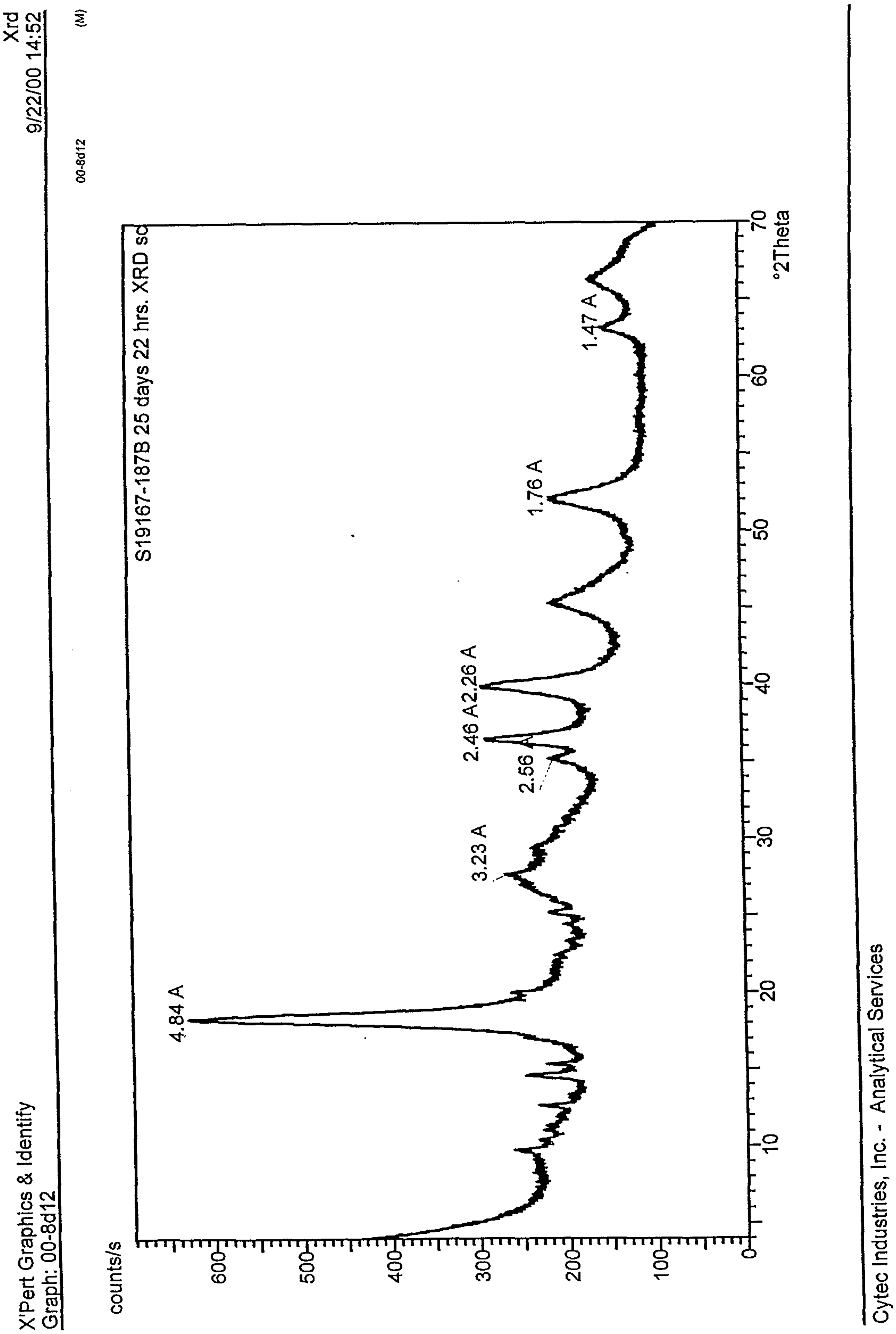
FIG 3.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